

## SYMPOSIUM ON PROCESSING AND PRODUCT SELECTIVITY OF SYNTHETIC FUELS

Presented before the Division of Fuel Chemistry  
American Chemical Society  
Washington, D.C., August 23-28, 1992

### ASSAY OF DIESEL FUEL COMPONENTS PROPERTIES AND PERFORMANCE

by Jimell Erwin  
Southwest Research Institute  
P.O. Drawer 28510  
San Antonio, TX 78228  
(512) 522-2389

#### Introduction

The increasingly stringent restrictions on exhaust emissions from diesel fuel powered vehicles pose a challenge for both existing petroleum fuels and proposed fuels from alternative sources. The EPA regulation limit governing particulates reduced to 0.25 g/bhp-hr in 1991 for trucks and to 0.1 g/bhp-hr for city buses in 1993. In 1994, the limit will drop to 0.1 g/bhp-hr for all vehicles. It is expected that Canada will adopt the same limits at a later date and Mexico will have similar standards for urban vehicles. EPA has not prescribed the method for meeting the emissions requirements for diesel engines. Engine manufacturers have performed significant development on cleaner engines without meeting the proposed standard in all cases. EPA issued regulations that limit sulfur content of diesel fuel to 0.05 weight percent and imposed a minimum 40 cetane index to "cap" aromatics content at present levels.<sup>1</sup> The California Air Resources Board has also announced regulations effective in 1993 that control diesel fuel sulfur content to less than 0.05 weight percent plus aromatics to less than 10 volume percent.

The objectives in the current work included producing a consistent set of performance, emission, and composition measurements on a set of diesel fuel components distinguished by source and processing history emphasizing aromatics. The components were reduced in sulfur and aromatic content by pilot plant hydrogenation before distillation into selected ranges of boiling points. The resulting fractions of feedstocks and products were analyzed for chemical composition and physical properties that would be most revealing for ignition quality and particulate generation.

This report presents the results to date of this work in progress. With the broad objective of relating diesel exhaust emissions and performance to chemical composition and physical properties, the more specific concerns of the effect of alkane branching and aromatic substituents will be addressed later. The choice of starting materials will give insight about source and upgrading method as they affect ignition quality and emissions from different samples meeting the same limits on sulfur and aromatics but with different processing histories.

#### Background

Contemporary diesel fuel is a blend of several refinery streams chosen to meet specifications. The need to increase yield of transportation fuel from crude oil has resulted in converting increased proportions of residual oil to lighter products. This is accomplished by thermal, catalytic, and hydrocracking of high molecular weight materials rich in aromatic compounds. The current efforts to reformulate California diesel fuel for reduced emissions from existing engines is an example of the other driving force affecting refining practice. Although derived from petroleum crude oil, reformulated diesel fuel is an alternative to current specification-grade diesel

fuel, and this alternative presents opportunities and questions to be resolved by fuel and engine research.

It has been observed that sulfur and aromatics concentrations increase with boiling point. For example, lower concentrations of aromatics and sulfur typically occur in D-1 fuel whose boiling range of 300-550°F is lower than D-2 fuel with 350-650°F. What has not been shown is which of the highest boiling components are most responsible for particulate emissions or which components of refinery streams would benefit the most from processing to reduce emissions precursors. The approach used for determining the effects of fuel composition on engine behavior has been to blend or measure full boiling range fuels for engine tests. For instance, the work at the University of Wisconsin<sup>2</sup> and the University of Pennsylvania<sup>3</sup> found little effect on performance and emissions attributable to fuel composition. Other studies had different results. Weidmann found that fuel properties have a small, measurable effect on emissions using a VW 1.67 liter, 4-cylinder engine.<sup>4</sup> Hydrocarbon emissions were found to be a function of fuel cetane number with volatility exerting a stronger influence for low cetane number fuels. Particulate formation was a strong function of fuel density and distillation range.

Fortnagel et al., found HC, NOx, CO, and a particulate emissions to be subject to aromatic content in a Mercedes Benz, prechamber-type engine.<sup>5</sup> A study by Gairing found large effects on exhaust emissions and fuel consumption attributable to fuel properties.<sup>6</sup> The diversity of these results is typical of the literature and emphasizes the strong influence that the engine type has on emissions from a given fuel. These studies were also performed with full-boiling fuels that made no attempt to segregate fuel properties by boiling range. Cookson attempted to determine the effect of hydrocarbon type composition on the diesel index (Method IP21) and the cetane index (ASTM D976) in 54 fuels, again using full-boiling materials.<sup>7</sup>

The approach to be used in the current work will attempt to improve on the resolution of previous studies done with full-boiling test fuels by examining the four starting materials in narrow fractions of the diesel fuel boiling range. We will then correlate the resulting measurements with emissions and performance indicators.

## Experimental

**Materials** ➤ Of the refinery streams blended into diesel fuel, the higher boiling and more aromatic ones are implicated in particulate and hydrocarbon emissions. Accordingly, feedstocks for this study were chosen to include products from resid conversion and gas oil cracking. The test components chosen were:

- full-boiling straightrun diesel (SRD)
- light cycle oil from catalytic cracking (LCO)
- light coker gas oil (LCGO)
- coal-derived Fischer-Tropsch distillate (FT)

The parentheses enclose the abbreviated designations used in this paper. The opportunity to include the highly paraffinic FT liquid extended the objectives to see the effect of a material which might provide future solutions to diesel emission problems. These four materials were characterized by a set of laboratory analyses as shown in Table 1.

**Processing** ➤ The four feedstocks were processed to reduce sulfur and aromatics then distilled into analytical samples. The processing and distillation sequence is shown in Figure 1. The LCO and LCGO were hydrogenated at two severities to reduce sulfur to 0.05 M% and aromatic concentration (by ASTM D1319) to 10 V%. The SRD was naturally low in sulfur and was hydrotreated at one severity to reduce aromatics to 10 V%. The FT required no hydrogenation. The process variables for the hydrogenations are summarized in Table 2.

TABLE 1. FEEDSTOCK PROPERTIES						
Test	ASTM Method	Straight Run Diesel	Lt. Cycle Oil	Lt. Coker Gas Oil	Fischer-Tropsch	
Density	D 1298	0.8458	0.9490	0.8676	0.7770	
Specific Gravity		35.8	17.6	31.6	50.6	
°API		0.8453	0.9485	0.8671	0.7767	
g/ml						
Distillation, °F		D 86				
IBP/5%	353/428		367/457	385/420	368/396	
10/30%	466/523		476/509	435/462	407/449	
50/70%	551/581		536/573	492/528	502/550	
90/95%	635/657		634/656	574/590	592/606	
EP	672		689	608	620	
Carbon, Wt%	D 3178	86.82	88.84	85.18	84.92	
Hydrogen, Wt%		13.31	9.84	12.58	15.12	
Sulfur, Wt%	D 2622	0.052	0.69	1.41	0.003	
Hydrocarbon Type, Vol %	D 1319					
Aromatics		23.6	75.45	52.4	0.9	
Olefins		1.0	3.64	5.9	0.9	
Saturates		74.7	20.91	41.7	98.2	
Viscosity @ 40°C	D 445	3.52	3.16	2.56	2.42	
@ 100°C		1.34	1.20	1.10	1.05	
Refractive Index @ 20°C	D 1218	1.4718	1.5537	1.4797	1.4342	
Cetane Index	D 976	52.6	26.1	39.3	75.4	
	D 4737	54.6	23.89	38.9	81.4	
UV Aromatics Analysis	TOTAL MONO DI TRI	11.4	43.7	15.7	0.2	
Wt% Aromatic Carbon		4.3	6.3	8.4	0.0	
		5.8	28.3	5.9	0.0	
		1.3	9.1	1.4		
Cloud point, °C/°F	D2500	1/34	-10/14	Too dark	-20/-4	
Pour point, °C/°F	D 97	-1/30	-12/10	-30/-22	-20/-4	
Aniline point, °C/°F	D 611	73.0/163	9.8/50	47.6/118	92.8/199	
Smoke point, mm	D 1322	17.2	6.2	13.3	+35	

Each of the four feedstocks and their five products were distilled under vacuum into congruent (corresponding cut point) boiling range fractions. The following boiling point ranges were selected for the cuts:

Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6	Fraction 7
IBP -	440° -	480° -	520° -	560° -	600° -	640° - EP
440°F	480°F	520°F	560°F	600°F	640°F	

Approximately 40 liters of each material were charged to a stainless steel kettle and column, which was operated along the lines of a ASTM D1160 distillation. The resulting 63 samples were further subsampled for separation by ASTM D2549 into saturates and aromatics fractions.

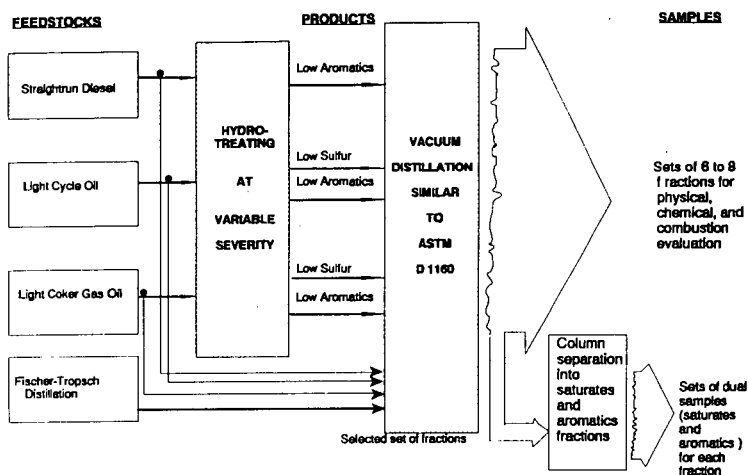


Figure 1. Sequence of Processing for the Diesel Fuel Assay

TABLE 2. PROCESSING PARAMETERS					
	T <sub>av</sub> , °F	P <sub>tot</sub> , psig	Feed, gal-hr <sup>-1</sup>	H <sub>2</sub> , SCFH	LHSV, hr <sup>-1</sup>
STRAIGHT RUN DIESEL					
High severity - low aromatics	630	1500	1.6	60	1.03
LIGHT CYCLE OIL					
Low severity - low sulfur	710	650	1.9	110	1.05
High severity - low aromatics	686	2300	0.74	130	0.41
LIGHT COKER GAS OIL					
Low severity - low sulfur	650	600	2.2	140	1.22
High severity - low aromatics	676	2200	0.98	117	0.56

Combination of adjacent cuts were made in the middle of the boiling range to limit the number of samples submitted for instrumental analysis. These combinations are indicated by the pairs and triples of sample numbers in brackets in Table 3.

**Analyses** ➤ The set of laboratory measurements listed in Table 1 are being applied to each of the 63 fractions made by vacuum distillation. The list includes two measures of aromatic content, D1319 and the UV method.<sup>8</sup> The fluorescent indicator analysis (ASTM D1319) is widespread in its use and included in emissions regulations. It is regularly applied to diesel fuel samples, although the method is designed for depentanized gasoline, and relies on measurements of column length taken up by saturates, olefins, and aromatics made visible by fluorescent dye. The volume percent aromatics determined this way can be affected by cycloparaffins or polar materials.

The UV method compares sample absorbance at selected wavelengths with reference spectra of solutions of aromatics composed of representative compounds in the diesel boiling range. Since the absorbance is proportional to the aromatic rings, weight percent aromatic carbon is reported without regard to substituents. Both methods are indirect; so instrumental analysis by GC/MS and NMR are planned.

The samples will be rated for ignition quality in a constant volume combustion apparatus (CVCA).<sup>9</sup> A single shot of sample is injected into a shaped combustion temperature at controlled temperature and pressure. The temperature, pressure, and stoichiometry of the fuel/air mixture causes the gas mixture to autoignite. When the sample ignites and burns, it results in a pressure rise, which is automatically measured. The ignition delay time from injection to measured pressure rise for various temperatures and reference materials has been correlated with measured cetane numbers for estimating the cetane number of samples. All 72 samples (4 feedstocks, 5 products, & 63 fractions) will be tested in the CVCA.

Engine experiments will be performed with a single cylinder, direct injected, variable compression ratio engine (VCR).<sup>10</sup> The cylinder head can be moved during operation to adjust compression ratio thus allowing knock measurements to be made, which are necessary for measuring cetane number. The piston and intake port are being modified to match contemporary configurations designed to comply with 1991 diesel engine emission standards. Measurements will include cetane number, fuel efficiency, pressures traces, heat release rate, and exhaust emissions of CO, CO<sub>2</sub>, O<sub>2</sub>, NO, NO<sub>2</sub>, C, and unburned hydrocarbons. Selected samples will be tested in the VCR engine.

## Results

The processing, distillation, and laboratory analyses are complete, while the instrumental analyses and CVCA measurements continue. The VCR engine is being modified to reflect contemporary design before the engine experiments take place. Table 3 presents some of the measurements on the 63 fractions to date. Density (specific gravity), abbreviated boiling range, and aromatic composition are given in the table, however, each fraction has received the full analysis listed in Table 1. The number of fractions distilled from each feedstock and product vary in number depending on the boiling range of the starting material.

The results for aromatic composition of the LCO are presented in the series of graphs of Figure 2. This series of graphs is representative of the changes made by hydrogenation. The total aromatic carbon was reduced moderately in concentration as the sulfur was reduced by low severity treatment. The distribution of aromatics decreased most in the highest boiling point fractions, which display the most tricyclic compounds. A similar decrease is noted for dicyclic aromatics, but monocyclics increase across the boiling range. The explanation for this increase will await the ASTM D2425 results to confirm the trend, but in addition to creating corresponding cycloparaffins from the two- and three-ring aromatics, the hydrogenation opened rings in the multicyclics to form alkylbenzenes distributed throughout the lower boiling ranges.

The trend for high severity hydrogenation to limit total aromatics showed the greatest decrease in polycyclics. The overall reduction in monocyclic aromatics was slightly greater for higher boiling ranges. These changes are expected to reduce emissions and are projected to improve ignition delay as shown in Figure 3.

The plot of cetane index *versus* 50% recovered temperatures (T50) by D86 in Figure 3 was made by two estimating methods; ASTM D976 and D4737. Both correlations use density and T50, but in different ways. D976 uses API gravity and T50 in two terms, while D4737 uses specific gravity and T50 in four terms. Furthermore, the new, four-term correlation used a larger fuel matrix including cracked components and shale oil to develop its correlation. D4737 made lower estimates of cetane number in the front end of the boiling

**TABLE 3. PARTIAL RESULTS FOR DISTILLATION FRACTIONS**

Property	Feed	#1	#2	#3	#4	#5	#6	#7	#8
<b>STRAIGHT RUN DIESEL</b>									
Sp. Gravity	0.8458	0.8146	0.8445	0.8483	0.848	0.845	0.847	0.859	0.863
Dist. T10/T50	466/551	338/404	465/480	486/498	514/523	544/550	578/584	617/622	666/673
T90/EP	635/672	452/475	501/515	516/529	542/556	564/576	597/610	634/643	687/698
Arom	Tot/Mono	11.4/4.3	12.4/7.9	13.6/4.6	13.3/4.4	12.5/4.3	10.9/4.0	8.7/3.1	17.1/5.7
C Wt%	Di/Tri	5.8/1.3	4.4/0.1	8.6/0.4	8.5/0.4	7.4/0.8	5.7/1.2	3.7/1.8	3.5/2.7
<b>LOW A SRD</b>									
Sp. Gravity	0.8280	0.7892	0.8251	0.8373	0.8368	0.8304	0.8203	0.8314	0.8373
Dist. T10/T50	442/539	241/278	386/404	440/452	482/494	530/538	567/577	615/620	673/683
T90/EP	622/664	323/351	438/455	474/488	510/526	552/562	587/597	631/641	699/715
Arom	Tot/Mono	3.3/3.0	7.8/7.7	5.8/5.6	5.0/4.6	3.6/3.2	2.6/2.2	1.5/1.3	1.1/0.9
C Wt%	Di/Tri	0.3/0.0	0.1/0.0	0.3/0.0	0.4/0.0	0.4/0.0	0.3/0.0	0.2/0.0	0.2/0.0
<b>LIGHT CYCLE OIL</b>									
Sp. Gravity	0.9490	0.8849	0.9147	0.9321	0.9440	0.9541	0.9685	0.9979	
Dist. T10/T50	476/536	384/410	447/459	483/490	515/522	548/552	583/588	643/651	
T90/EP	634/689	443/492	473/492	499/518	531/544	562/575	596/614	677/734	
Arom	Tot/Mono	43.7/6.3	42.5/26.7	55.3/14.5	57.2/6.8	60.6/5.1	46.1/4.1	41.2/3.3	46.7/0.1
C Wt%	Di/Tri	28.3/9.1	15.0/0.8	39.8/1.0	49.6/0.8	53.9/1.6	39.3/2.7	28.6/9.3	10.4/36.2
<b>LOW S LCO</b>									
Sp. Gravity	0.9200	0.8849	0.9082	0.9153	0.9230	0.9352	0.9484	0.9497	
Dist. T10/T50	462/518	370/424	444/467	472/488	503/519	543/557	595/603	650/663	
T90/EP	614/682	469/510	502/544	521/548	549/572	579/595	617/630	702/738	
Arom	Tot/Mono	35.8/16.6	29.1/23.3	35.4/22.9	35.8/20.4	36.9/16.7	34.1/11.8	32.9/6.8	32.0/2.4
C Wt%	Di/Tri	15.0/4.2	5.8/0.0	12.5/0.0	15.1/0.3	19.0/1.2	19.6/2.7	17.5/8.6	9.5/20.1
<b>LOW A LCO</b>									
Sp. Gravity	0.8628	0.8479	0.8623	0.8676	0.8708	0.8745	0.8703	0.8448	
Dist. T10/T50	419/488	362/384	412/422	446/454	477/486	514/520	547/552	606/620	
T90/EP	581/657	406/419	432/453	470/488	499/514	530/544	561/574	669/715	
Arom	Tot/Mono	3.5/3.1	5.6/5.4	3.6/3.4	4.1/3.7	3.9/3.4	2.9/2.5	2.5/2.0	1.4/1.0
C Wt%	Di/Tri	0.4/0.0	0.2/0.0	0.2/0.0	0.4/0.0	0.5/0.0	0.4/0.0	0.5/0.0	0.4/0.0
<b>LIGHT COKER GAS OIL</b>									
Sp. Gravity	0.8676	0.8403	0.8565	0.8740	0.8871	0.8927	0.9094		
Dist. T10/T50	435/492	395/410	446/456	486/495	530/537	565/571	603/609		
T90/EP	574/608	429/461	473/491	508/526	547/565	580/595	624/645		
Arom	Tot/Mono	15.7/8.4	10.9/8.5	12.6/7.4	13.7/6.3	14.5/6.0	13.8/5.3	14.4/4.7	
C Wt%	Di/Tri	5.9/1.4	1.7/0.7	4.4/0.8	6.4/1.0	7.2/1.3	6.8/1.7	6.1/3.6	

**TABLE 3. PARTIAL RESULTS FOR DISTILLATION FRACTIONS  
(Continued)**

Property	Feed	#1	#2	#3	#4	#5	#6	#7	#8
<b>LOW S LCGO</b>									
Sp. Gravity	0.8463	0.8184	0.8299	0.8403	0.8524	0.8628	0.8697		
Dist. T10/T50	427/476	360/389	399/415	432/447	473/484	512/523	567/577		
T90/EP	552/599	427/457	442/467	473/492	504/526	539/550	598/624		
Arom	Tot/Mono	10.5/8.2	10.0/9.4	10.9/9.8	10.2/8.4	11.0/8.2	11.2/7.7	11.4/7.2	
C Wt%	Di/Tri	2.3/0.0	0.6/0.0	1.1/0.0	1.8/0.0	2.8/0.0	3.4/0.1	3.5/0.7	
<b>LOW A LCGO</b>									
Sp. Gravity	0.8393	0.8203	0.8265	0.8324	0.8418	0.8490	0.8498	0.8524	
Dist. T10/T50	436/491	374/390	404/417	437/448	474/483	508/516	548/556	595/602	
T90/EP	576/612	414/430	440/466	468/485	503/520	530/546	566/574	622/644	
Arom	Tot/Mono	3.3/3.0	4.5/4.3	3.9/3.7	3.6/3.3	3.5/3.1	3.3/2.9	2.7/2.3	2.2/1.8
C Wt%	Di/Tri	0.3/0.0	0.2/0.0	0.2/0.0	0.3/0.0	0.4/0.0	0.4/0.0	0.4/0.0	0.4/0.0
<b>FISCHER-TROPSCH</b>									
Sp. Gravity	0.7770	0.7538	0.7633	0.7710	0.7783	0.7853	0.7913	0.7989	
Dist. T10/T50	407/502	355/373	397/416	438/453	478/490	522/531	558/566	607/615	
T90/EP	592/620	420/456	452/474	475/488	507/521	545/557	579/589	628/638	
Arom	Tot/Mono	0.2/0.2	0.4/0.4	0.3/0.3	0.2/0.2	0.2/0.2	0.1/0.1	0.1/0.1	0.1/0.1
C Wt%	Di/Tri	0.0/0.0	0.0/0.0	0.0/0.0	0.0/0.0	0.0/0.0	0.0/0.0	0.0/0.0	0.0/0.0

range and higher estimates in the back end. These calculations will be compared with the CVCA and VCR results for verification, but the fractions at highest boiling ranges increased the most in cetane index. This is consistent with the results of Weidmann et al, for full-boiling test fuels.

### Conclusions

It has been observed that a consistent set of narrow-boiling samples was unavailable and this work will fill the need, however, this study is in the initial stages permitting few conclusions. The early results obtained to date suggest that the dominant effects for both emissions (by virtue of polycyclic aromatic distribution) and performance (considering the relative increase in cetane index) will be in the higher boiling point fraction. Further instrumental analyses of hydrocarbon type composition and the combustion studies will add to our understanding. The current results offer guidance on where in the boiling range the strongest effects can be found.

The improvement in the high end of the boiling curves is significant for the emissions and performance benefits that were obtained and for resource utilization. It has been suggested generally and implemented in California to reduce the limit for T90 for the D-2 specification. Careful control of upgrading may reduce the necessity to curtail T90 thereby leaving more of each blendstock in the diesel fuel boiling range.

## Acknowledgements

This work has been supported by the U.S. Department of Energy Office of Conservation and Renewable Energy Alternative Fuels Utilization Program (AFUP), John A. Russell, manager, first through its operations at the Oak Ridge National Laboratory, Dr. R.L. Graves, project representative then at the National Renewable Energy Laboratory, Kenneth R. Stamper, program manager representative.

The concept of the study was suggested by Norman R. Sefer the first project manager of the AFUP Alternative Fuel Center at Southwest Research Institute. The able technical staff for the processing included: C.C. Cover, D.L. Hetrick, P.M. Rainwater, and G.R. Segura. The engine combustion studies will be conducted by Dr. T.W. Ryan III. The numerous tables and typescript were prepared by Evangelina S. Martin.

## REFERENCES

1. "Fuel Quality Regulations for Highway Diesel Fuel Sold in 1993 and Later Calendar Years", Federal Register, Vol. 54, No. 163, August 24, 1989.
2. Foster, D.E., Dimplefeld, P.M. Boggs, D.L., Bair, R.E., and Borman, G.L., "The Effects of Fuel Composition on Ignition Delay in Homogeneous Charge and Direct Injection Compression Ignition Engines", Final Report, Contract DE-AC05-84OR21400, U.S. Department of Energy, Alternative Fuels Utilization Program, Report No. ORNL/Sub/84-89677/1, November 1987.
3. Buzza, T.G., and Litzinger, T.A., "A Comparison of Three Coal-Derived, Middle Distillate, Synthetic Fuels in a Single Cylinder DI Diesel Engine", SAE International Fuels & Lubricants Meeting, Toronto, Canada, November 2-5, 1987.
4. Weidmann, K., Menrad, H., Reder, K., and Hutchenson, R.C., "Diesel Fuel Quality Effects on Exhaust Emissions", SAE International Fuels & Lubricants Meeting and Exposition, Portland, Oregon, SAE Paper No. 881649, October 10-13, 1988.

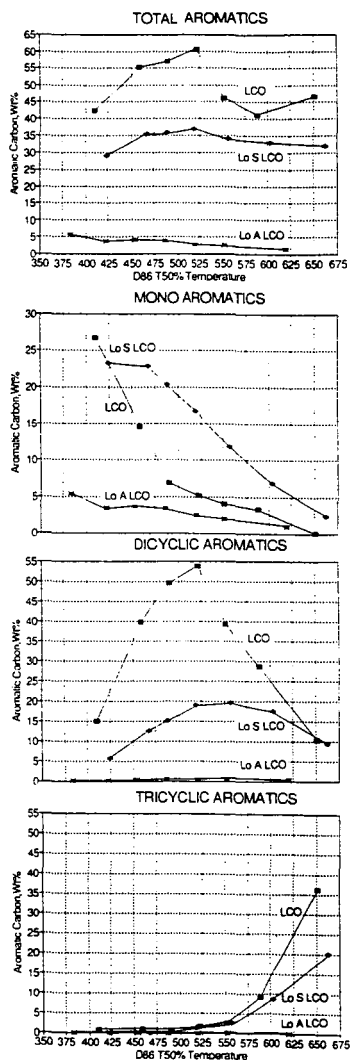


Figure 2. LCO Aromatics Distribution



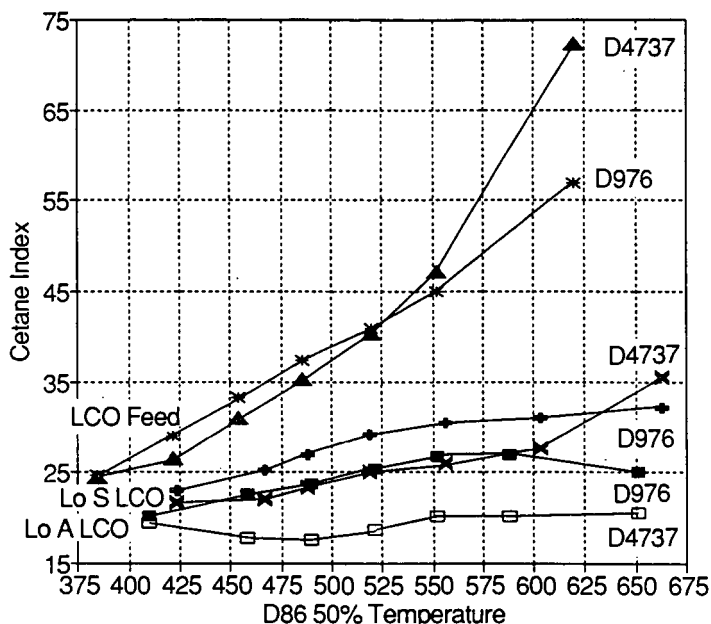


Figure 3. Cetane Index by ASTM D976 & D4737 vs LCO D86 50% Temperature

- Fortnagel, M., Gairing, M., Wagner, W., "Verbesserung des Diesel-Motors-Verschlechterung des Diesel-Kraftsoffs - ein Eiderspruch", VDI Berichte No. 466, 1983.
- Gairing, M., "Anforderungen and Diesel-Kraftsoffqualitat-heute und in Zukunft", VDI Berichte No. 559, Emissionsminderung Automobilabgase - Dieselmotoren - VDI Verlag 1985.
- Cookson, D.J., Lloyd, C.P., and Smith, B.E., "Investigation of the Chemical Basis of Diesel Fuel Properties", Energy and Fuels 2, 854-860, 1988.
- Kohl, K.B., Bailey, B.K., Newman, F.M., and Mason, R.L., "Chemical Analysis of Aromatics in Diesel Fuels", report for California Air Resources Board A932-125, 20 June 1991.
- Ryan, T.W. III, "The Development of New Procedures for Rating the Ignition Quality of Fuels for Diesel Engines", U.S. Army Belvoir RD&E Center, Interim Report 223, BFLRF, Southwest Research Institute, December 1986.
- Ryan, T.W. III, "Ignition Delay as Determined in a Variable Compression Ratio, Direct Injection Diesel Engine", SAE Paper 872036, November 1987.